

Water Quality Sampling for the Chihuahuan Desert Laboratory: A Study Proposal

Introduction

Carlsbad Caverns National Park is part of the regional Capitan aquifer system. Evapotranspiration and rapid surface runoff causes most infiltration to occur in the bottom of drainages. Except for a perched water system that feeds surface seeps and springs, the park is a recharge area for the regional groundwater system (Tallman, 1993). The water table is located at 1,065m (3,200 ft.) above sea level, or 365m (1,100 ft.) below the natural entrance of Carlsbad Cavern.

Water occurs in the Cavern as drips from active speleothems, or as pools fed by drips and seeps. Inactive speleothems in the cavern indicate past flow into areas that are now dry. The distribution of hydrologically active and inactive areas has been well documented and correlates well with fracture systems and changes in reef facies (Brooke, 1996).

Once water reaches the subsurface, flow is largely controlled by bedrock lithology, the presence of large fracture systems, and open karst conduits (Brooke, 1996; Hill, 1987). Groundwater movement in the backreef units is dominated by lateral flow along bedding and along the contact between the Tansill and Yates formations. The massive Capitan limestone is characterized by downward flow in vertical fracture systems. All of the rock units have been modified by cave development and may have preferential flow paths through open karst conduits. Major fracture systems have controlled the orientation of cave passages and can allow rapid infiltration from the surface into the cave.

Many of these fracture systems underlie parking lots and other potential sources of contamination. In general, it takes three to five months for contaminated water to reach the cave from the surface. However, flow through the major fracture systems can be much more rapid (Chapman et al., 1992; Williams, 1983).

Objectives

Conduct long-term water quality-monitoring to establish baseline conditions of cave pools.

Compare water quality between cave pools evaluating proximity to trail and surface contaminate pathway factors.

Analyze storm surface runoff after precipitation events.

Methods

Students will collect water samples from sites in Carlsbad Cavern and from caves administered by the United States Forest Service. The National Park Service will periodically collect samples from other caves and share data with students. The key to student success is the appreciation for systematic environmental sampling and analytical chemistry. Based on Park management responses, there has never been a systematic water sampling strategy for Carlsbad Cavern. In addition, students will practice standard sampling techniques, use standard testing methods, analyze data and prepare a written evaluation.

Students will collect water samples from the following sources: (1) three pools close to trails and (2) three pools 30 to 40 feet from the trail. People track in contaminants, which can accumulate in cave pools. In the year 2000, trails will be vacuumed instead of washed to reduce contamination of cave pools. This study will measure changes in contaminant levels resulting from these changed management practices. Bacteria levels in pools will be compared. Nitrate levels will be monitored in all pools. Metals will also be monitored. Runoff samples from the downhill side of the parking lot will be tested. It is believed the highest concentrations of contaminants will be in the runoff approximately 10 minutes after the start of a rain. The National Park Service will regularly monitor pools near the surface before and after significant rainfall events that are greater than 0.57inches (14.478mm).

Students will analyze water samples (in the classroom and at the Carlsbad Environmental Monitoring and Research Center) for key water quality indicators such as: coliform, suspended sediments, alkalinity, conductivity, dissolved oxygen, nitrates, phosphates and sulfates. Students will randomly test water samples for heavy metals at Carlsbad Environmental Monitoring and Research Center. Comparative studies will be conducted between the pool water in the Carlsbad Cavern and protected pools at other locations in the park.

Students will assist park personnel in pool restoration. There are several cave pools that have been contaminated by park maintenance practices. This project will involve removing the pool silt and coins thrown in pools by visitors. Students will compare sulfate, copper and zinc levels in pools before and after restoration (silt and coin removal).

To enhance student observational and methodical skills, pool measurements (length, width and depth) will be used to calculate pool volume and pool surface area, and predict “recharge rate” after restoration.

Samples will be collected from the following pools:

- Devil's Spring-in the Main Corridor – located just beyond the twilight zone

- Trail Side Pool- (also known as Signature Pool) – located a few switchbacks down from the "Cave Climate" sign
- Green Lake – located along the King's Palace tour route
- Longfellow's Bathtub – located in the Big Room just past Rock of Ages
- Shelf Pool -- located in the Big Room near the shortcut
- Red Pool – located in the Big Room near the shortcut

Field Water Quality Measurements

Cave pool water levels and depth will be determined at the time of sampling. Field instruments will be utilized to measure water temperature, conductivity, dissolved oxygen and pH. Water temperature will be measured using an electronic sensor calibrated to within 1°C. Conductivity is measured in microSiemens/centimeter ($\mu\text{S}/\text{cm}$) by use of a conductivity meter. A microSiemen is the same as a micromho. Conductivity of a water sample is a measure of electric current. The more impurities (total dissolved solids) in water, the greater the electrical conductivity and the amount of total dissolved solids. To convert the electrical conductivity (microSiemens/cm) to total dissolved solids (ppm), the conductivity must be multiplied by a factor which varies between 0.54 and 0.96. The value of this factor depends upon the type of dissolved solids. A widely accepted value, when not determining the type of dissolved solids, is 0.67. $\text{TDS (ppm)} = \text{Conductivity (microSiemens/cm)} \times 0.67$. pH (pH units) and dissolved oxygen (mg/L) will be measured with a multimeter and will be calibrated with water temperature. This can be done in a classroom laboratory setting.

Field sample collection, preservation and quality control will follow standard procedures.

Sampling Techniques and Precautions

The objective of sampling is to collect a portion of material small enough in volume to be transported conveniently and handled in the laboratory while still accurately representing the material being sampled. This implies that the relative proportions or concentrations of all pertinent components will be the same in the samples as in the material being sampled, and that the sample will be handled in such a way that no significant changes in composition occur before the tests are made. Environmental sampling will follow American Standards Testing Methods (ASTM) Standards, and testing will follow Standard Methods.

Students will obtain the best sample by careful collection. In general, students will collect samples near the center of the pond and below the surface. Students will use only clean containers. Rinse the collection container with the water to be sampled before collecting the sample. For general collections, use 100mL plastic bottles. With a gloved hand, lower the bottle and allow it to partially fill with water. Once water enters the bottle, retrieve the bottle and swirl the water around to clean it out. Discard this

water and repeat the procedure once more. Do not use distilled water to rinse the bottle. This approach alters chemical composition. Likewise, the sampling bottle should never be used for cleaning or other purposes, as this will also affect sampling results. Using a latex-gloved hand, the student will submerge the bottle in the middle of the pool, being careful not to let the bottle sink or stir up the bottom sediment. To obtain a sample, the bottle will be allowed to fill fully (most analyses) or leave space for aeration, mixing, etc. (microbiological analysis), then bring the bottle out of the water.

A maximum of eight students and two Principle Investigators will participate in any water testing in the cave. During collection of samples, one student will leave the paved trail where pools are closest to the trail. In cases where the pool is at the bottom of a steep incline or distant from the trail a second student may leave the paved trail and act as a "go between" to reduce impact to the cavern floor. Cross contamination between pools will be eliminated by using a new glove and clean bottle for each pool. Equipment used, such as probes for the pH meter and conductivity meter, will be rinsed with deionized water and dried between pools. Another student will be located in advance of the pool along the trail to interpret the water sampling activities to cavern visitors passing by.

Particular care is required when processing samples for trace metal analyses. The student will make a record of every sample collected and identify every bottle by attaching an inscribed tag or label. Record sufficient information to provide sample identification at a later date, as well as the name of the sample collector, date, hour, exact location, water temperature and other data such as weather conditions, water level, etc. Provide space on the label for the initials of those assuming sample custody and for the time and date of transfer. Fix sampling points with detailed descriptions on maps; this will permit identification by other persons and will remove the need to use memory or personal guidance. Pools are subject to considerable variations from normal causes such as seasonal stratification, rainfall and runoff. Choose location, depth and frequency of sampling depending on local conditions.

Data will be recorded carefully on standardized field data sheets with reference to place and time. Water samples will be marked with a label with site name, location, identification number, date/time, sampler, preservative and analysis required.

Other precautions will take place as identified by the collection permit.

Quantity of Samples

During a one-year period, water quality sampling will be conducted monthly. During the second year, sampling will be conducted in spring, winter and fall and every other week during the peak visitor season.

Collect samples for most physical and chemical analyses. For certain determinations, larger samples may be necessary.

Table 1 indicates the volume required for specific analyses of routine sampling. Separate samples should be taken for chemical, bacteriological and microscopic examinations.

Table 1

Determination	Container	Minimum Sample
Alkalinity	P	200mL
Conductivity	On-site	--
Hardness	P(A)	100mL
Metals, general	P	100mL
Total Nitrogen	On-site whenever possible	100mL
Oxygen, dissolved	On-site	--
pH	On-site	--
Phosphate	G(A)	100mL
Solids, dissolved	P	500mL
Sulfate	P	100mL
Temperature	On-site	--

Key

P	=	plastic
G	=	glass
(A)	=	rinsed with 1 + 1HNO ₃

Bottling Technique and Preservation of Samples

Under most circumstances, perform pH, total nitrogen, electrical conductivity, dissolved oxygen, and temperature tests at the selected study site. If necessary, tests can be performed in the laboratory. The dissolved oxygen protocol can be completed in the lab after the dissolved oxygen has been stabilized in the field. If samples for these tests are to be transported, do the pH and total nitrate test within two hours of collection. Do tests for electrical conductivity and alkalinity within 24 hours.

Use the following procedure to bottle sample water and transport it to the classroom:

1. Use plastic bottles to collect most samples. A glass bottle rinsed with 1 + 1HNO₃ for phosphate sample. (See Table 1 for container type and minimum sample size.)
2. Label the bottle with site name, the date and time of collection, water temperature and any other data that may be needed for correlation.
3. Rinse the bottle and cap with sample water.
4. Fill the bottle with sample water until the water forms a dome shape at the top of the bottle so that, when a cap is put on, no air is trapped inside.
5. Seal the cap of the bottle with masking tape. Note: Tape serves as a label and an indicator of whether the bottle has been opened. Tape should NOT be in contact with the water sample itself.
6. Store samples in a refrigerator at about 4⁰ C until they can be tested.

7. Once the seal is broken, perform all the measurements during the same lab session when possible.

Samples for testing at Carlsbad Environmental Monitoring (CEM) will be collected in 250mL bottles prepared by the CEM staff. Samples will be stabilized with five (5) drops of concentrated HNO_3 and placed on ice. Samples will be stored in a refrigerator at about 4°C until the samples can be transported and turned over to CEM staff.

Safety

- Consult the Material Safety Data Sheets (MSDS) that come with kits and buffers. Also, consult the local school district's and NPS safety procedure guidelines.
- When using kits with chemicals, latex gloves and safety goggles are recommended.

Laboratory Testing

Recommended Sample Preservation

Bottle	Measurement	Preservative	Holding Time	Analysis
#1 (125mL)	Hardness ^{*1} Total Metals	HNO_3 to pH<2 HNO_3 to pH<2	6 months	ICP
#2 (125mL)	Total Nitrogen Total PO_4^{-3}	Frozen Frozen	28 days 28 days	Colorimetric
#3 (125mL)	Alkalinity ^{*2}	Cool to 4 Degrees C	14 days	Titration

^{*1} Hardness is calculated representing mg/L as CaCO_3 . Hardness = $2.497(\text{Ca mg/L}) + 4.118(\text{mg/L Mg})$ based on ICP values (ion chromatography may be used on a .45 μ filtered sample to determine caution levels).

^{*2} Note conductance, dissolved oxygen, pH and temperature will all be analyzed immediately on site.

Regardless of the water quality parameters being measured, complete stability for every constituent can never be achieved. At best, preservation techniques can retard the chemical changes that inevitably continue after the sample is removed from the pool. Water quality tests on laboratory samples will be completed within holding time limits. Laboratory procedures should follow accepted methods, as per ASTM STANDARDS, current edition, STANDARD METHODS for the Examination of Water and Wastewater, and Hach Water Analysis Handbook.

Pool water samples for heavy/trace metal will be collected in acidified (pH<2 nitric acid washed) plastic bottles. Samples will be unfiltered and stored at 4°C. Heavy/trace metal will be analyzed by inductively-coupled plasma emission spectrometry and atomic absorption spectrometry.

Pool water samples for basic ion chemistry and total nitrogen, total phosphorus and alkalinity will be collected in plastic bottles. Laboratory analysis will use standard methods (ANPHA 1989) and will be expressed in mg/L. Ion analysis for Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , PO_4^{3-} , NO_3^- , and SO_4^{2-} will be conducted using ion chromatography (Dionex Model 2020). Total phosphorus and total nitrogen will be analyzed (Autoanalyzer) on filtered (0.45 μm) water samples (stored frozen). Laboratory standard methods used for measuring alkalinity include colorimetric titration to pH 4.5 and expressed as the equivalent concentration (mg/L) of CaCO_3 . Total hardness will be determined using ICPE concentrations of calcium and magnesium where hardness equals $2.497(\text{mg/L Ca}) + 4.118(\text{mg/L Mg})$.

Specific conductance and pH will be measured immediately after taking unfiltered water samples. The specific conductivity measured will be temperature-compensated (corrected to 25°C). They will be calibrated using an NADP reference standard. Conductance will be measured in mhos/cm (1mhos = $10^6 \mu\text{mhos}$). The pool pH will be measured with a calibrated meter fitted with a probe accurate in the pH 7 to 8 range. The pH meter must be calibrated each testing day with pH 4 and 7 buffer solutions from NADP. The pH readings can be assumed to be accurate to 0.1 pH units.

Definitions

Specific conductivity refers to the ability of the medium to conduct an electrical current. Conductance is the inverse of resistance and is measured as the reciprocal of ohms, or mhos (standard deviation up to 10% can be expected). Conductivity data can help characterize the overall pool chemistry. Such data is particularly useful when both pH and conductivity are controlled by dissolved inorganic ions such as bicarbonates (McDonalds 1991). Conductivity is an indicator of dissolved solids, which change the physical and chemical nature of the water (osmotic pressure).

Since pH varies with different temperature and carbon dioxide concentrations, measurements will be made in the field immediately after taking the water samples. The pH is defined as the molar (number of moles per liter) concentration of hydrogen ions $[\text{H}^+]$ in water. Because the range of hydrogen ion concentrations in water can range over 15 orders of magnitude, pH is defined on the logarithmic scale as: $\text{pH} = \log 1/[\text{H}^+]$ = $-\log [\text{H}^+]$.

Alkalinity is a measure of the buffering capacity (power to neutralize acids (hydrogen ions, H^+)). The presence of carbonates (limestone formations) is the most common cause of alkalinity in natural waters.

Water hardness is a measure of the bivalent metallic ions dissolved in water. Calcium and magnesium contribute to the hardness properties of water (ion chromatography may be used on a 0.45 μm filtered sample to determined caution levels).

Dissolved oxygen concentrations refer to the rate of diffusion of dissolved (molecular) oxygen across a membrane, and the resulting generation of an electrical signal. If the electrodes are properly maintained and calibrated, the potentiometric method is

significantly accurate for nearly all field monitoring (accuracy of + or -0.1mg L⁻¹ precision of + or -0.05mg L⁻¹) (APHA 1989).

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